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NEW TYPES OF HYDROCARBON SYNTHESIS FROM CARBON MONOXIDE AND HYDROGEN

Ya. T. Eydus

/A Digest./

This digest reviews the progress which has taken place during the past 10 years in work pertaining to the synthesis of CO and H_2. Most of the material presented by Eydus refers to works published outside the USSR. However, in the present digest, only work done in the USSR has been covered.

I. CATALYSTS

1. Function of Individual Catalyst Components

An optimum relationship between the hydrogenating component (Ni, Co, Fe), the component inducing polymerization (i.e., the difficultly reducible oxides ThO_2, MnO, MgO, Cr_2O_3, Al_2O_3, ZnO, SiO_2, etc., which are added to the catalyst and at the same time serve as promoters and carriers) or the component which has a dehydrogenating effect and at the same time induces polymerization (ThO_2, Cr_2O_3, Al_2O_3, ZnO) must exist for the most efficient catalyst (6). B. N. Dolgov (7) has found that nickel by itself or on a carrier has no activity whatever with respect to the synthesis. Among binary mixtures 100 Ni: (1-10) Al and 100 Ni: (1-10) Mn the most active catalyst was 100 Ni: 4.5 Al, in the presence of which the yield of liquid hydrocarbons amounted to 130 milliliters per one cubic meter of the initial gas. This catalyst was very unstable and lost 70-80 percent of its initial activity in 50-75 hours. Binary catalysts Ni-Mn, Ni-Cu, Ni-Cr, Ni-Fe, Ni-Co, etc., were found to be totally inactive, while a quaternary catalyst on kaolin was found to be the most active; at a volume velocity of 100 liters per one liter of catalyst per hour, it gave a yield of 175-185 milliliters per cubic meter at 195 degrees centigrade.

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V. Karzhavin, Yu. Polyakin, I. Klimenko, and E. Karzhavina (8, 6) perfected a catalyst having the composition 100 Ni: 20 Mn: 10 Al_2O_3 : 100 infusorial earth (kieselguhr) and obtained with it yields reaching 180-200 milliliters per cubic meter. They ascribe the hydrogenating effect to Ni or Co, the polymerizing to MnO, MgO, or ThO_2, and the dehydrating effect to Al_2O_3, Cr_2O_3, or ThO_2. At the same time, they assume that the formation of hydrocarbon chains takes place at the interphase boundary metal-polymerizing oxide. In this connection, they attach great importance to the structure of the polymerizing oxides.

In their opinion, the crystal structure of the oxide must correspond as closely as possible to that of Cc and Ni. Also, the components of the catalyst must be properly oriented with respect to each other. In other words, the regulation of interphase boundaries is particularly important, because it determines the reproducibility of catalysts. The authors see a confirmation of this view in the effect which the degree of oxidation of manganese has on the catalyst Ni-Mn-Al_2O_3 - infusorial earth when that catalyst is prepared by coprecipitation of basic carbonates (8). The controlled oxidation of Mn was carried out by aeration rather than the usual method of adding hydrogen peroxide. In this manner the formation of Mn_2O_3, an oxide having a structure similar to that of carbonates, was assured, thus achieving the necessary mutual orientation.

I. B. Rapoport and E. N. Polozhintseva have investigated fused catalysts on an extensive scale as well as precipitated nickel catalysts (9). They found that a binary Ni-Al catalyst, although unstable, was very active, giving a liquid hydrocarbons yield of 180-190 milliliters per cubic meter. On the basis of this result, they concluded that the aluminium promoter of a nickel catalyst not only has a dehydrating function but also that of polymerizing CH_2 radicals. This was contrary to V. A. Karzhavin's view. Rapoport and Polozhintseva found that Ni-Mg was less active.

The highest activity and stability was shown by a multicomponent catalyst giving a maximum yield of 250 milliliters per cubic meter and an average yield of 193 milliliters per cubic meter.

In work done abroad on Co and Ni kieselguhr carrier catalysts, it could be shown that a considerable part of the catalyst surface is occupied by the promoter. This resembles closely the results obtained earlier by Eydus on Fe catalysts (10).

2. Precipitated Co - Ni Catalysts

/Nothing other than foreign research./

3. Iron Catalysts

Since 1939, a considerable amount of work has been done on the substitution of the cheaper Fe catalyst for Co and Ni. Investigations in this field have been carried out both in the USSR (11) and abroad. In 1942-43, Ya. T. Eydus and collaborators compared the activities of Fe-Cu catalysts having the basic composition 100 Fe: 25 Cu: 2 K_2CO_3: 125 Kisatibi kieselguhr (12). The effects of the method of preparation (precipitation or thermal decomposition), of the precipitating agent (potassium carbonate or sodium carbonate), and of the nature of the activating component (2 percent with reference to the weight of the iron of MnO, MgO, Al_2O_3, or ThO_2) have been studied. All these catalysts, as distinguished from Ni and Co in the absence of Cu, do not require reduction at high temperatures with hydrogen, resembling in that respect Co-Cu-Mn (13, 14). They are activated by the initial gas mixture at the temperature of the synthesis, this temperature being 230-260 degrees centigrade in the case of a Fe catalyst and 170-210 degrees centigrade in the case of a Ni or Co catalyst. Apparently the metallic copper formed first catalyzes the formation of metallic Fe or Co in the process of reduction of the catalyst by the gas mixture.

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The results obtained in this instance show that both the type of metal oxide which had been added and the method of preparation have a definite effect on the activity of the catalyst. As a rule, precipitated catalysts are more active than those obtained by thermal decomposition and catalysts precipitated with potassium carbonate are more active than those which had been precipitated with sodium carbonate. An exception is the catalyst containing MgO; sodium carbonate is a better precipitant here than potassium carbonate. The catalyst containing MnO is more active when the method of thermal decomposition is used.

Among the investigated catalysts the most active are those prepared by the method of precipitation with potassium carbonate and containing ThO_2 and MnO - also the catalyst containing MgO and prepared by precipitation with Na_2CO_3. The catalysts which do not contain promoters are much inferior to the promoter-containing catalysts prepared by the precipitation method. Experiments did not confirm published data on the desactivating effect of Al_2O_3 and ThO_2 on a precipitated Fe-Cu catalyst (Y. Murata, S. Makino, and S. Tsuneoka, Sci. Pap. Inst. Phys. Chem. Res., 1939, Vol XXXV, 348) or the activating effect of Al_2O_3 when it is added to Fe-Cu-Mn after precipitation (S. Makino, H. Koide, and Y. Murata, Sci. Pap. Inst. Phys. Chem. Res., 1940, Vol XXXVII, 350). On the contrary, aluminium oxide and thorium oxide were found to have an activating effect. The maximum yield of liquid hydrocarbons obtained with a potassium carbonate precipitated and promoter-containing MnO catalyst was 79-80 milliliters per cubic meter. The Fe-Cu catalysts which have been tested exhibited very low stability.

Further investigation (15) indicated that the optimal contents of ThO_2 and K_2CO_3 is 1-2 percent and 2 percent respectively referred to the weight of Fe. Various infusorial (diatomaceous) earths were tested as catalyst carriers. The best performance was obtained with Inza diatomite, marshalite, and Kisatibi and Taman' diatomites (yields of 85.1 81, 74, and 51.8 milliliters per cubic meter respectively). The maximum yield obtained with these catalysts amounted to 143 milliliters per cubic meter, this figure referring to combined liquid and solid hydrocarbons (16). The average yield of water in the reaction is 5-16 milliliters per cubic meter, which indicates that the reaction proceeds principally under transfer of CO oxygen to CO_2, as formulated in reaction scheme A.

$$2nCO + nH_2 \longrightarrow C_nH_{2n} + nCO_2$$

(A)
$$2nCO + (n+1)\,H_2 \rightarrow C_nH_{2n+2} + nCOH_2$$

This is typical of Fe catalysts, while on Ni and Co catalysts the reaction proceeds mainly under formation of water according to scheme B, so that the yields of water reach 180 milliliters per cubic meter (17).

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

(B)
$$nCO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

Investigation of the liquid and solid reaction products (16) has shown that the fraction boiling between 38 degrees centigrade and 150 degrees centigrade comprises 51 percent by weight of the total gasoline and 30 percent by weight of the total yield of liquid and solid hydrocarbons. The fraction having the boiling range 150-200 degrees centigrade comprises 16 percent and 10 percent of these weights, respectively, and the fraction boiling in the range 200-250 degrees centigrade, 34 percent and 20 percent. Oil boiling above 250 degrees centigrade amounts to 18 percent and solid paraffin to 13-14 percent of the total yield of hydrocarbons, not counting gas oil. A comparison of the gasolines boiling below 150 degrees centigrade which had been obtained on Ni, Co, and Fe catalysts indicates the higher degree of saturation of gasoline obtained on a Fe catalyst. The content of unsaturated hydrocarbons amounts to 12, 31, and 80 percent for Ni, Co,

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and Fe catalysts respectively. One must take into consideration, however, that the degree of unsaturation also depends on the composition of the initial gas mixture, and that the optimum composition of the latter is $1CO:2H_2$ for Ni and Co catalysts and $1CO:1H_2$ for Fe catalysts.

The solid paraffin obtained in the presence of a Fe catalyst melted at 58 degrees and could be distilled in the range 225-295 degrees at 15 millimeters (16). The molecular weights of its fractions (molecular weights 381-578) corresponded to the normal paraffins C_{32} - C_{41}, while the melting temperatures (51.5-65.5 degrees centigrade) indicated the normal paraffins C_{27} - C_{31}. The divergence is due to the presence of branched hydrocarbons and possibly to traces of oil.

While a slower rate of heating of a Fe-Cu catalyst in the reductive regeneration with hydrogen leads to a more active catalyst (18), the situation is reversed with regard to Ni catalysts. According to V. A. Karzhavin (6, 8), there is a considerable increase in the activity of a Ni-Mn-Al_2O_3 catalyst if it is reduced at a high rate, and the reduction is started directly at the high temperature of 450 degrees centigrade. This is in accordance with S. Z. Roginskiy's theory of supersaturation (19, 20).

An investigation of Fe-Cu catalysts was carried out by B. N. Dolgov (7), who found that the catalyst 4 Fe - 1 Cu deposited on kaolin gives a yield of liquid hydrocarbons amounting to 40-60 milliliters per cubic meter. However, this catalyst was found to be unstable. Fe-Cu 100 Fe: 2-5 Ni and 100 Fe: 2-5 Co proved to be still less stable. The highest activity was shown by the catalyst 100 Fe: 2 Ni, which gave a yield of 96 milliliters per cubic meter, but the activity dropped by 75 percent after 24 hours of operation.

An extensive investigation of the activity and stability of Fe-Cu catalysts was conducted by B. P. Vaynshteyn and I. B. Rapoport (21). They found that the best promoter is MnO and the second best MgO. Addition of a mixture of MgO and Al_2O_3 has a negative effect. The best alkaline activating agents are silicates. With the use of this type of activator a mixture containing 4 percent of Mn gave a stable catalyst yielding 137 milliliters per cubic meter at 230 degrees centigrade from gas having the composition 100 : 1.5 H_2; 362 hours of operation lowered the activity to only an insignificant extent. Kaolin proved to be the best carrier. Active catalysts were obtained by precipitating nitrates at 100 degrees centigrade with a 20-percent excess of potassium carbonate.

Fe catalysts can also be used in the synthesis of hydrocarbons at elevated pressures, as illustrated by work published in the US and Japan. At high pressures water is formed in considerable quantities, as a result of the reaction. B. N. Vaynshtein and I. B. Rapoport have obtained with a Fe catalyst at 10 atmospheres a yield reaching 144.9 milliliters of liquid hydrocarbons per cubic meter accompanied by a yield of water amounting to 33-66 milliliters per cubic meter (21). With increased volumetric speed the yield drops.

In view of the exothermic nature of the reaction, heat regulation, and efficient heat transfer in cooling, the reactor plays a considerable part in this synthesis. It has been assumed that the efficiency of the conversion is reduced by the counteracting effect of reaction products. A multistage conversion with removal of already formed reaction products between the stages has actually resulted in improved yields. Proper heat regulation in the reactor is also important, however. Thus, V. A. Karzhavin (6) in studying the dependence of the hydrocarbon yield on the length of the catalyst layer was able to show that the yield as related to the length of the catalyst layer passes through a sharp maximum (43 grams per liter per hour as compared with an average yield of 13 grams per liter per hour). This is due to a temperature gradient disposed along the length of the catalyst layer in such a manner that the maximum output corresponds to the highest temperature. Karzhavin is of the

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opinion that these inhomogeneous temperature conditions limit the extent of the reaction and that the reaction products have no counteracting effect. A solution of the problem would then be proper regulation of temperatures in the catalyst layer rather than a multistage process.

4. Ruthenium Catalysts

5. The Industrial Cobalt Catalyst (22)

6. Synthesis in the Liquid Phase

(Sections 5 and 6 describe German industrial procedures. The descriptions are based on data taken from German and US published reports and on German patent claims.)

7. Reduction of Catalyst Activity

II. MODIFICATIONS OF THE PROCESS

1. Synthesis of Isoparaffins

This is mainly an account of experimental and development work on the subject done at Muelheim (Ruhr) during the war. Some investigations reported upon here deal not only with the synthesis of isoparaffins, but also with that of aromatic and naphthene hydrocarbons from CO and H_2 (23).

2. Synthesis of Aromatics

(Description of work done at Muelheim, Ruhr)

3. Sinol Process

(Description of a German process for the synthesis of alcohols from CO and H_2.)

III. NEW REACTIONS OF CARBON MONOXIDE WITH OLEFINS

1. "Oxo" Synthesis

2. Condensation of Carbon Monoxide with Olefins under Hydrogenation ("Hydrocondensation")

The "hydrocondensation" of carbon monoxide with olefins was discovered by Ya. T. Eydus, N. D. Zelinskiy, and K. V. Puzitskiy (24-27) independently of the German "Oxo" synthesis. The point of similarity with the "Oxo" synthesis is that a mixture of CO, H_2, and olefin is converted. As distinguished from the "Oxo" synthesis, the reaction is carried out at atmospheric pressure and hydrocarbons rather than oxygen containing derivatives are formed. To illustrate, ethylene is converted to the extent of 80-90 percent into liquid hydrocarbons in such a manner that only 15-20 percent are hydrogenated to ethane.

The products are mainly aliphatic hydrocarbons of predominatly straight chain structure. The content of oxygen compounds is insignificant. The hydrocarbon fraction of the total liquid product is composed of saturated and unsaturated aliphatic hydrocarbons having a wide boiling range (27-420 degrees centigrade). The proportion of unsaturated compounds increases from 34

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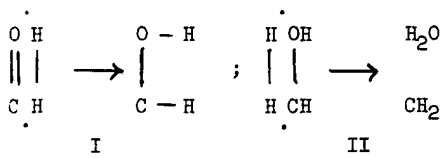
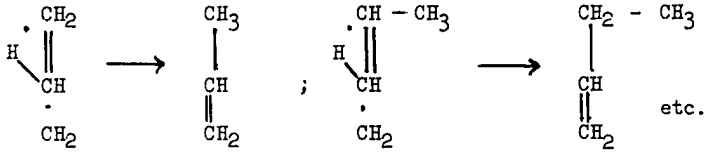
percent to 67 percent of the total in passing from the heavy fraction boiling at 255-343 degrees centigrade to the light fraction boiling at 27-60 degrees centigrade. An exact fractionation yields hydrocarbons having even (C_6, C_8) and odd (C_5, C_7, C_9) numbers of carbon atoms in the molecule. The content of oxygen compounds in the oil phase of the condensate is 2-3 percent, in the aqueous phase 10 percent. The principal product containing oxygen is propyl alcohol. The water phase and the oil phase contain 2 percent and 1 percent of aldehydes, respectively. The only aldehyde identified is propionic aldehyde. In addition to that, a 1.5-degrees content of organic acids, with propionic acid comprising 70 percent of the total acid content, was found in the water resulting from the reaction. This refers to the conversion of ethylene.

The hydropolymerization of olefins under the action of a small quantity (4-7 percent) of carbon monoxide was discovered by Ya. T. Eydus, N. D. Zelinskiy, and N. I Ershov (27, 28). This reaction is closely related to the "hydrocondensation." Products of the same type as in the last-mentioned reaction are obtained.

The process of hydrocondensation of CO with C_2H_4 under formation of olefins can be formulated as follows:



I II

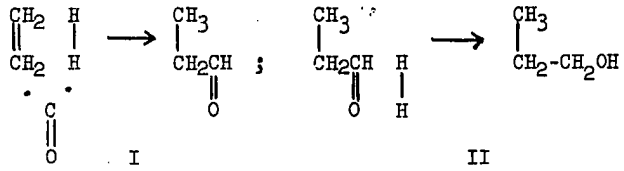


III IV

In I, CO is partly hydrogenated with the formation of an unstable intermediary group. The latter is then further hydrogenated to a CH_2 radical (II). The CH_2 radical polymerizes with the olefin under formation of the next highest homolog. The condensation of CO with C_2H_4 does not take place in the absence of H_2, which indicates that CH_2 radicals are actually formed and play an essential role in the reaction.

As mentioned above, the oxygen compounds formed to an insignificant extent in the hydrocondensation essentially contain only three atoms of carbon, i. e., they are formed by the interaction of one molecule of CO with one molecule of C_2H_4. The formation of oxygen compounds can be expressed by the following scheme:

a)



I II

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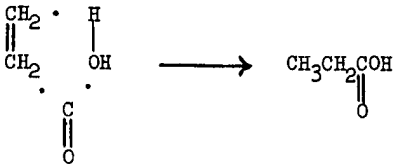
b)



The above text covers progress made in the synthesis of hydrocarbons from CO and H_2, in the field of reactions of CO + H_2 with olefins, and in this branch of carbon monoxide chemistry in general during the past 10 years. Questions pertaining to the production of the initial gas mixture CO - H_2, the mechanism of the fundamental reaction, and the properties and utilization of reaction products will form the subject of a subsequent publication.

BIBLIOGRAPHY

1. Ya. T. Eydus, Uspekhi Khimii (Progress of Chemistry), 1938, Vol VII, 1714-1754.
2. Ya. T. Eydus, Uspekhi Khimii, 1938, Vol VII, 1801-1857
3. Ya. T. Eydus, Uspekhi Khimii, 1940, Vol IX, 673-681
4. B. Dolgov, Methods of Chemical Utilization of Carbon Oxides, 1936
5. Symposium, "Synthesis of Liquid Fuel," edited by B. A. Kasanskiy, introduction by N. D. Zelinskiy, Moscow, 1940
6. V. A. Karzhavin, Uspekhi Khimii, 1947, Vol XVI, 328-352
7. B. N. Dolgov, Scientific Contributions of the Leningrad State University (Chemical Series), 1945, Vol VII, 56
8. V. Karzhavin, Yu. Polyakin, I. Klimenko, and E. Karzhavina, Byull. NITO, Gastopprom (Bulletin of the Scientific Technical Engineering Society, Gas and Fuel Industry), 1946, Vol I, 5
9. I. B. Rapoport, E. N. Polozhintseva, Trudy VNIGI (Contributions of the All-Union Scientific-Research Institute for Gas and Synthetic Liquid Fuel), 1948, Vol I, 162
10. Ya. T. Eydus, Iz. AN SSSR, OKhN (News of the Academy of Sciences, USSR, Division of Chemical Sciences), 1945, No 1, 62
11. I. Cherniy, Byull. NITO, Gastopprom, 1946, Vol III, 27
12. Ya. T. Eydus, P. F. Epifanskiy, L. V. Petrova, N. V. Elagina, and S. B. Al'tshuller, Izv. AN SSSR, OKhN, 1943, No 2, 145
13. Ya T. Eydus. T. L. Fedichkina, B. A. Kazanskiy, and N. D. Zelinskiy, Izv. AN SSSR, OKhN, 1941, No 1, 34
14. A. M. Rubinshtein, N. A. Pribytkova, B. A. Kazanskiy, N. D. Zelinskiy, Izv. AN SSSR, OKhN, 1941, Vol I, 41
15. Ya. T. Eydus, and N. V. Elagina, Izv. AN SSSR, OKhN, 1943, Vol IV, 305
16. Ya. T. Eydus, ZhOKh (Journal of General Chemistry), 1946, Vol XVI, 869
17. Ya. T. Eydus, B. A. Kazanskiy, and N. D. Zelinskiy, Izv. AN SSSR, OKhN, 1941, Vol I, 27
18. Ya. T. Eydus, ZhOKh, 1946, Vol XVI, 875
19. S. Z. Roginskiy, ZhFKh (Journal of Physical Chemistry), 1941, Vol XV, 708
20. S. Z. Roginskiy, ZhPKh (Journal of Applied Chemistry), 1944, 97
21. B. P. Vaynshteyn and I. B. Rapoport, VNIGI, 1948, Vol 1, 181
22. S. V. Tatarskiy, K. K. Papok, and E. G. Semenido, Neft. Khoz. (Petroleum Economy), 1946, Vol II, 52; Vol 1, 54
23. D. Orochko, Byull. NITO, Gastopprom, 1946, Vol III, 27
24. Ya T. Eydus and K. V. Puzitskiy, DAN (Reports of the Academy of Sciences), 1946, Vol LXV, 35
25. Ya. T. Eydus, N. D. Zelinskiy and K. V. Puzitskiy, Izv. AN SSSR, OKhN, 1949, Vol I, 110

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Sanitized Copy Approved for Release 2011/08/17 : CIA-RDP80-00809A000600310329-2

Sanitized Copy Approved for Release 2011/08/17 : CIA-RDP80-00809A000600310329-2

50X1-HUM

26. Ya. T. Eydus, N. D. Zelinskiy, and K. V. Puzitskiy, Izv. AN SSSR, OKhN, 1949, Vol III, 326
27. N. D. Zelinskiy, DAN, 1948, Vol LX, 235
28. Ya. T. Eydus, N. D. Zelinskiy, and N. I. Ershov, DAN, 1948, Vol LX, 599

/NOTE: In addition to the above, 93 non-Russian references have been listed./

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